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FINAL REPORT

to

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Bolling AFB, Washington DC 20332**

by

Lionel M. Raff and Donald L. Thompson

**Oklahoma State University
Department of Chemistry
Stillwater, Oklahoma 74078**

**Project Title: Theoretical Studies of Heterogeneous Reactions
in Silicon CVD**

Period Covered: November 1, 1985 to October 31, 1988

**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
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MATHIAS J. KILMER
Chief, Technical Information Division**

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I. INTRODUCTION

A program of theoretical/computational research has been carried out to determine the relative importance and the fundamental dynamical behavior of various elementary processes that are postulated to play a role in the silicon vapor deposition (CVD) from silane. The emphasis of the work has been on computing results that are comparable to experimental data. Thus, a lot effort has been expended to develop accurate and realistic potential-energy surfaces to describe the forces in the processes we have studied. We have used these potential-energy surfaces to compute rates of the various elementary processes by a variety of techniques. Much of the research was done using standard classical trajectory methods. We also employed Monte Carlo variational phase-space and transition-state theories, which have been developed in this research program, to study processes that occur on timescales that make trajectory methods intractable. In the course of this work, we have further refined these techniques to provide theoretical methods that give more accurate results and that require less computer time. For example, we have developed methods for correcting for tunneling effects in multidimensional systems and methods for reducing the computational magnitude of problems by employing various approximations for "bath" effects.

The chemical emphasis of the research has been on homogeneous and heterogeneous silicon hydride systems. The types of elementary processes we have studied include:

- ~ Unimolecular dissociation of isolated gas-phase molecules and radicals.

- ~ Silicon clustering.
- ~ Gas-surface scattering.
- ~ Chemisorption.
- ~ Heterogeneous reactions on silicon crystals.
- ~ Effects of surface coverage on gas-surface processes.
- ~ Diffusion on silicon surfaces.
- ~ Bimolecular gas-phase reactions.
- ~ Tunneling in H-atom diffusion on silicon surfaces.

II. Grant Personnel

The personnel associated with the AFOSR research project include:

Co-Principal Investigators:

- * Professor Donald L. Thompson
- * Professor Lionel M. Raff

Postdoctoral Research Associates:

- * Dr. Raji Viswanathan (11/1/82-5/1/85)
- * Dr. I. NoorBatcha (11/1/85-1/1/86)
- * Dr. Paras Agrawal (7/1/86-10/31/88)

Graduate Students:

- * Ms. B. M. Rice (11/1/85-11/1/87), Ph.D. 1987.
- Ms. Nancy S. Gettys ((6/1/84-1/1/86)
- Mr. Huadong Gai (8/1/87-12/1/87)
- Mr. Michael Jezcerak (6/1/86-present)

Undergraduate Students:

- Ms. Mia Musset (9/1/88-present)
- * Mr. Craig Arnold ((6/1/86-9/1/86)

* Indicates those individuals who were partially or fully supported by the grant.

III. Publications and Oral Presentations

The following papers reporting research supported by AFOSR-86-0043 have been published, submitted for publication, or are being prepared for publication:

- C. Arnold, N. S. Gettys, D. L. Thompson, and L. M. Raff,
"Theoretical Studies of Vibrationally Assisted Reactions of the O_3 -NO van der Waals Complex,"
J. Chem. Phys. 84, 3803-3813 (1986).
- I. NoorBatcha, L. M. Raff, D. L. Thompson, and R. Viswanathan,
"Dynamics of Unimolecular Dissociation of Silylene,"
J. Chem. Phys. 84, 4341-4346 (1986).
- D. L. Martin, D. L. Thompson, and L. M. Raff,
"Theoretical Studies of Termolecular Thermal Recombination of Silicon Atoms,"
J. Chem. Phys. 84, 4426-4428 (1986).
- L. M. Raff, I. NoorBatcha, and D. L. Thompson,
"Monte Carlo Variational Transition State Theory Study of Recombination and Desorption of Hydrogen on Si(111),"
J. Chem. Phys. 85, 3081-3089 (1986).
- B. M. Rice, L. M. Raff, and D. L. Thompson,
"Quasiclassical Trajectory Study of the Unimolecular Dissociation of Ammonia,"
J. Chem. Phys. 85, 4392-4399 (1986).
- B. M. Rice, L. M. Raff, and D. L. Thompson,
"The Dynamics of H_2 scattering and Dissociative Chemisorption on a Si(111) Surface,"
J. Chem. Phys. 86, 1608-1615 (1987).
- L. M. Raff and D. L. Thompson,
"Reply to the 'Comment on: Silane Pyrolysis and the insertion of Silylene into Molecular Hydrogen,'"
J. Chem. Phys. 86, 3058 (1987).
- L. M. Raff and D. L. Thompson,
"Theoretical Studies of Elementary Processes in the Chemical Vapor Deposition of Silicon from Silane,"
Proceedings of the 1987 ASME/JSME Thermal Engineering Joint Conference,
Vol. 1, edited by P.J. Marto and I. Tanasawa, 1987, pp. 603-611.
- P. M. Agrawal, L. M. Raff, and D. L. Thompson,
"Effect of the Lattice Model on the Dynamics of Dissociative Chemisorption of H_2 on a Si(111) Surface,"
Surface Science 188, 402-420 (1987).
- H. Gai, D. L. Thompson and L. M. Raff,
"Trajectory Study of the Formation and Decay of Silicon Trimer Complexes in Monomer-Dimer Collisions,"
J. Chem. Phys. 88, 156-162 (1988).
- M. Jezercak, P. M. Agrawal, C. B. Smith, and L. M. Raff,
"Wave Packet Studies of Gas-Surface Inelastic Scattering and Desorption Rates,"
J. Chem. Phys. 88, 1264 (1988).
- P. M. Agrawal, D. L. Thompson, and L. M. Raff,
"Computational Studies of Heterogeneous Reactions of SiH_2 on Si(111) Surface system"
Surface Science 195, 283-306 (1988).

- B. M. Rice, L. M. Raff, and D. L. Thompson,
"Dynamics of Adsorption/Scattering of Atomic Hydrogen on Partially Covered Si(111) Surfaces"
Surface Science 198, 360-399 (1988).
- P. M. Agrawal, D. L. Thompson, and L. M. Raff,
"Computational Studies of $\text{SiH}_2 + \text{SiH}_2$ Recombination Reaction Dynamics on a Global Potential Surface Fitted to *Ab Initio* and Experimental Data,"
J. Chem. Phys. 88, 5948-5962 (1988).
- B. M. Rice, L. M. Raff, and D. L. Thompson,
"Diffusion of H-Atoms on a Si(111) Surface with Partial Hydrogen Coverage: Monte Carlo Variational Transition-State Theory with Tunneling Correction,"
J. Chem. Phys. 88, 7221-7231 (1988).
- P. M. Agrawal, D. L. Thompson, and L. M. Raff,
"Trajectory Studies of Unimolecular Reactions of Si_2H_4 and SiH_2 on a Global Potential Surface Fitted to *Ab Initio* and Experimental Data,"
J. Chem. Phys. 89, 741-750 (1988).
- L. M. Raff,
"Projection Methods for Obtaining Intramolecular Energy Transfer Rates from Classical Trajectory Results: Application to 1,2-Difluoroethane"
J. Chem. Phys., 89, 0000 (1988)
- M. Jezercak, P. M. Agrawal, D. L. Thompson, and L. M. Raff,
"A Perturbation-Trajectory Method for the Study of Gas-Surface Collision Dynamics,"
J. Chem. Phys., submitted.

The following oral presentations have been made at meetings or universities based on work supported by this grant:

- "Theoretical studies of chemical reactions on silicon surfaces," Chemistry Division, Naval Research Laboratory, Washington, D.C., October 20, 1986.
- "Heterogeneous Surface Processes in Silicon CVD", ACS Symposium on Surface Chemistry Induced by Energized Particles and Lasers, New York City, NY, April, 1986.
- "Theoretical Studies of Gas-Surface Scattering and Surface Chemistry", Sandia National Laboratories, Albuquerque, New Mexico, January, 1987.
- "Dynamics of Adsorption/Scattering of Atomic Hydrogen on Partially Covered Si(111) Surfaces", Conference on Molecular Dynamics, Wheeling, West Virginia, July, 1987.
- "Theoretical Investigations of Homogeneous and Heterogeneous Reactions in the Chemical Vapor Deposition of Silicon from Silane," AFOSR Surface Chemistry Contractors Conference, Air Force Academy, Colorado Springs, Colorado, September 16-18, 1987.
- "Tunneling in H-Atom Diffusion on Partially H-Covered Si(111)," Department of Chemistry, Iowa State University, Ames, October 9, 1987.
- "Diffusion and Scattering of H-Atoms on Partially Hydrogen-Covered Si(111)," Department of Chemistry, Stanford University, March 31, 1988.

"Diffusion and Scattering of H-Atoms on Partially Hydrogen-Covered Si(111),"
Department of Chemistry, University of Texas, Dallas, April 27, 1988.

IV. Review of Research

A. Overview

We have been conducting a series of theoretical studies of the elementary homogeneous and heterogeneous processes involved in the chemical vapor deposition (CVD) of silicon from silane. The homogeneous gas-phase reactions investigated to date range from "simple" three-body clustering reactions of silicon atoms to extremely complex polymerization reactions. Heterogeneous surface processes involve the study of sticking, dissociative chemisorption, energy transfer, surface diffusion, relaxation effects to bulk modes, chemical reaction and tunneling effects on several different silicon surfaces. The chemistry involved in these events is, in many cases, very complex. Often, several competing reactions must be considered.

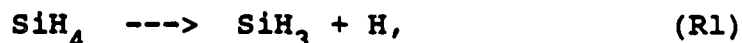
The intricacies of the reactions of interest in silicon CVD require that a variety of theoretical methods be used. Principal among these are variational transition-state methods such as those developed by Truhlar, Garrett, and coworkers[1] and by Voter and Doll[2], a variety of Monte Carlo methods, importance sampling techniques, classical trajectories, Langevin methods developed and implemented by Aldeman, Doll, and coworkers[3] and by Lucchese, Tully, and coworkers[4] as well as other surface relaxation procedures[5]. The necessity to develop sufficiently accurate potential-energy surfaces requires liberal use of ab initio SCF and CI methods and perturbation procedures such as Moller-Plesset fourth-order theory. In addition, semiempirical methods are often useful. Semiclassical procedures may be coupled with reaction path methods and variational transition-state theory or variational phase-space methods to

study surface tunneling effects.

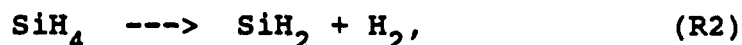
The general thrust of our work has been to determine the extent to which each of the above methods is useful in the examination of complex chemical systems such as those for silicon CVD and, where necessary, to develop suitable extensions of existing methods or entirely new procedures. In this section, we review our accomplishments to date. The methods employed and the principal results of each investigation are briefly summarized.

B. Homogeneous Reactions

Except at very low pressures, [6] the initiating reactions in the silicon CVD process involve the unimolecular decomposition of the starting reactant. For silane the principal reactions of interest are therefore



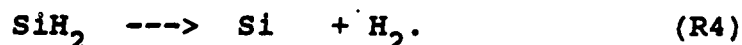
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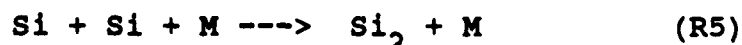
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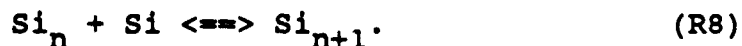
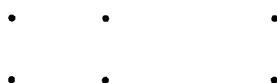
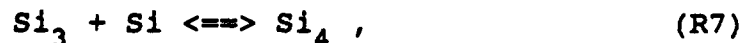
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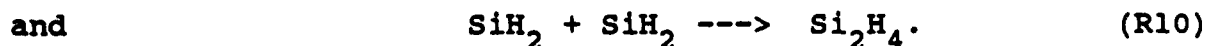
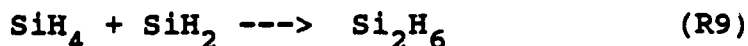
Once silicon atoms are formed via reaction R4, clustering processes are initiated. The initiation reactions may be either



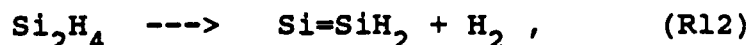
where M is any third body or via polymer decomposition pathways as described below. As soon as the Si₂ dimer is formed, further clustering occurs, that is,



The SiH₂ formed in reaction R2 may undergo a variety of polymerization reactions. The most important ones are probably



Once formed, these higher silanes and silenes may decompose to form Si_2 dimers thereby initiating the clustering reactions, i.e.



Coltrin, Kee, and Miller[7a] and Breiland, Coltrin, and Ho[7b] have suggested that reactions R9-R13 are the major mechanistic pathways leading to silicon dimer formation. These decomposition channels are all energetically open due to the exothermicity of reactions R9 and R10 which will be primarily released into internal modes of the polymer. The nature of the intramolecular energy transfer in these molecule will determine the important decomposition channels and their rates. Consequently, fundamental studies of the dynamics of intramolecular energy transfer in large polyatomics is of central importance in the understanding of these reactions.

The reactions dynamics, including rates, cross sections, and mechanisms, for reactions R1, R2, R3, R4, R5, R6, and R10 have been determined. Studies of reactions R11, R12 and R13 have also been completed. The unimolecular decomposition reactions of SiH_4 and SiH_2 , R1-R4, have been investigated using quasiclassical trajectories with Metropolis sampling and two classical variational phase-space methods.[8-10] The first of the variational phase- methods[9] uses an RRKM formalism but replaces the quantum-state counts with analogous classical sums over phase space. The calculated rate is then variationally minimized with respect to the location of the dividing surface. This procedure is based upon the work of Farantos, Murrell, and Hajduk[11], Bhuijan and Hase[12], and that of Noid, Koszykowski,

Tabor, and Marcus[13] who have shown that there is often excellent agreement between the exact quantal sums and the classical phase-space integrals. The second variational method[10] is an application of Doll's[2] generalization of Slater theory in which he has removed the assumption of normal modes and replaced the averaging over the normal mode vibrational phases with an average over the microcanonical ensemble. Doll used the method to examine the dissociation of four-atom clusters[2] and Adams[16] employed similar procedures to obtain vibrational predissociation rates for van der Waals clusters.

The studies of SiH_4 and CH_4 unimolecular decomposition[8-10] give a detailed comparison of the results of both variational methods with those obtained from classical trajectory calculations using a Metropolis sampling procedure to average over the reactant phase space. We have shown that the methods are in excellent agreement provided the rate is minimized with respect to the dividing surface at each energy considered. In addition, high-pressure limiting rates and microcanonical rates for reactions R1-R4 have been obtained.[8-10,15] Three-center dissociation reactions, R2 and R4, are found to be the major decomposition pathways. Both concerted eliminations and processes that resemble "half-collisions" are found to be important dissociation mechanisms.

We have extended the Monte Carlo variation phase-space theory(MCVPST) method to the calculation of microcanonical unimolecular decomposition rates out of specific rotational states.[16] This type calculation is a variant of that originally developed by Wardlaw and Marcus[17] who computed such rates using a transition-state procedure in which the the "transitional" modes are treated with Monte Carlo methods while the quantum states for the remaining degrees of freedom are counted directly. Hase and Wolf[18] and Miller and Brown[19] used classical trajectories in $(\text{H} + \text{C}=\text{C})$

and HO_2 systems, respectively, to evaluate angular momentum effects upon the reaction dynamics. Hase and Wolf found that orbital angular momentum is generally conserved upon passing from the potential-energy barrier to products while Miller and Brown found that angular momentum acts to reduce microcanonical rate coefficients beyond that predicted by a simple centrifugal barrier effect. We applied our MCVPST method to CH_4 decomposition on the ab initio potential surface developed by Duchovic, Hase, and Schlegel[20] and obtained results in qualitative accord with the previous findings reported by Wolf and Hase and by Miller and Brown. In general, it was found that the magnitude of the angular momentum effect decreases as the ratio of the rotational energy to the energy in excess of threshold decreases. Overall, the MCVPST procedure was shown to more than an order of magnitude more computationally efficient than corresponding classical trajectory calculations. Recently, Klippenstein and Marcus[21] have shown that for reactions with "loose" transition states, the quantum mechanical corrections (excluding tunneling) for the classical treatment of transitional modes is less than 2%.

Silicon clustering reactions, R5-R8, may play a crucial role in the overall silicon CVD mechanism. It has been found that the Si_2 dimer makes a significant contribution (up to 50%) to the total CVD rate provided the temperature is in excess of 1150 K and the carrier gas is helium.[7,21] In general, clustering is of great interest in a variety of systems.[23] We have therefore devoted considerable effort to its study in the silane system. As mentioned above, the steps leading to silicon dimers could be either reaction R5 or polymerization followed by decomposition as illustrated by reactions R9-R13.

An estimate of the three-body recombination rate for reaction R5 where $\text{M}=\text{Ar}$ has been obtained using the methods we

originally developed to examine three-body processes in the $H_2 + I_2$ reaction.[24,25] The results show that reaction R5 has a near-zero activation energy with a rate coefficient $6-9 \times 10^{13} \text{ cm}^6/\text{mol-s}$. Whether such three-body processes can effectively compete with a polymerization-decomposition pathway leading to Si_2 will depend upon the concentration of silicon atoms present, the pressure, and the rates for the elementary steps in reactions R9-R13 which are currently being examined.

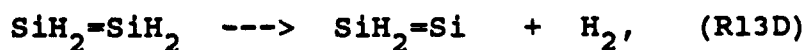
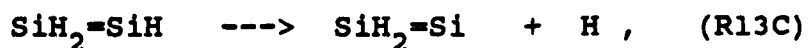
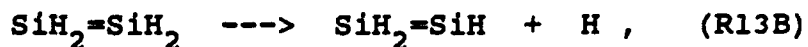
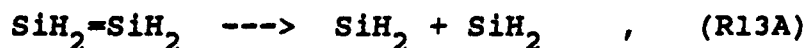
Once Si_2 is formed by either termolecular recombination or via a polymerization-decomposition route, further nucleation leading to higher silicon clusters is possible. We have recently calculated the cross sections and thermal rate coefficients for Si_3 formation, reaction R6, as well as the lifetimes for the internally excited trimers thus formed.[26] This reaction may be one of the crucial steps in nucleation processes leading to the formation of higher silicon clusters. At present, reaction R7 is under investigation using potential-energy surfaces fitted to the ab initio results recently reported by Raghavachari.[27]

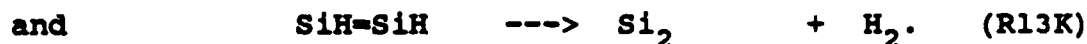
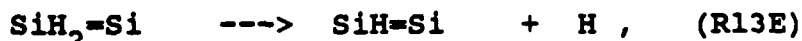
The essential step in these calculations is the formulation of an accurate potential-energy surface. To do this we have made use of ab initio results reported by Raghavachari[27] and by Peyerimhoff and Buenker.[28] In addition, we have utilized the experimental data reported by Chatillon et al.[29] and Huber and Herzberg.[30] Raghavachari[27] carried out CI and MP4 calculations using (6s,5p,2d,1f) basis sets for both equilibrium and non-equilibrium Si_3 geometries. Peyerimhoff and Buenker[28] have reported CI studies of the Si_2 dimer. They give potential energy curves for the ground and many of the excited electronic states. In order to utilize these results in a scattering study of the

dynamics, it is necessary to fit all of these data to a global representation of the surface. We have developed a general procedure for obtaining such fits. Our strategy is based upon the use of many-body terms, each of which is chemically and physically motivated. This type of procedure has now been used to obtain global surfaces for Si_3 , [26] Si_2H_4 , [31] and 1,2-difluoroethane. [32] For the Si_3 system, the calculated rms deviation of the energies obtained from the global surface from those reported by Raghavachari [27] is 0.117 eV. Equilibrium geometries and energies are essentially in exact accord with the ab initio results. [27] The Si_3 fundamental frequencies obtained from the global surface are within 37 cm^{-1} or less of those given by the MP4 calculations. Results for the Si_2H_4 potential surface are described below. In general, we feel that the fitting methods that have been developed are well-suited to use in complex systems such as those of importance in silicon CVD.

The thermal rate coefficients for reaction R6 are on the order of $10^{15} \text{ cm}^3/\text{mol-s}$ and show a negative temperature dependence at temperatures below 200 K. The Si_3 lifetimes are found to lie in the range 4.7×10^{-13} to $5.0 \times 10^{-11} \text{ s}$. [26]

The most complex gas-phase system that we have examined to date is the polymerization of two SiH_2 molecules to form disilene, reaction R10, followed by the subsequent decomposition of this molecule. [31] The decomposition modes of Si_2H_4 , which are represented by reaction R13, are actually very complex involving at least 11 channels, i.e.





Reactions R13B-R13H and R13J are the two- and three-center elimination processes leading to atomic and molecular hydrogen. Reactions R13I and R13K are four-center, 1,2-hydrogen elimination reactions leading to SiH=SiH and Si₂, respectively. The complexity of the system is obvious.

The formulation of an accurate potential-energy surface is clearly the most difficult step is the study of the reaction dynamics of this system. In principle, the total potential, V_T , may be written as a many-body expansion,

$$V_T = \sum_i^N V_i \quad ,$$

where the V_i are i -body terms and V_T includes the sum of all possible such terms. Murrell and coworkers[33] have made effective use of such an expansion for systems in which $N < 4$. For more complex systems, however, the many-body expansion becomes computationally intractable. As mentioned above, we have developed a general method for fitting global potentials to the results of ab initio calculations and experimental data. Our method employs a subset of many-body terms whose functional forms are based on physical and chemical considerations. These parametrized terms are then fitted by non-linear procedures to the available information on the system.

For the Si_2H_4 system, we have used the ab initio calculations reported by Ho, Coltrin, Binkley, and Melius[33,34], by Gordon and coworkers,[35,36] Binkley,[37] and Peyerimhoff and Buenker[28] as a basis for fitting a global potential. These studies use CI and MP4 methods to obtain bond enthalpies, equilibrium geometries, fundamental vibrational frequencies, and transition-state enthalpies for SiH_n and Si_2H_n ($n=0-6$) molecules. In addition, important experimental data has been obtained by Berkowitz et al.[38], Jasinski[39], and Inoue and Suzuki[40] all of which have been incorporated into the surface. The result is a global representation for the Si_2H_4 potential that consists of 18 many-body terms that physically describe the geometries, energies, and stretching, bending, and torsional motions for $\text{H}_2\text{Si}=\text{SiH}_2$, $\text{H}_2\text{Si}=\text{SiH}$, $\text{H}_2\text{Si}=\text{Si}$, $\text{HSi}=\text{Si}$, $\text{HSi}=\text{SiH}$, H_2 , SiH_2 , and Si_2 species as well as the barrier heights and reaction profiles for the reactions R13A-R13K.[41] In general, the equilibrium bond lengths and angles given by the global surface are in agreement with ab initio results to within 0.03 Å and 0.5° , respectively. The calculated exothermicities for reactions R13A-R13K are in excellent agreement with previous MP4 calculations[28,33-37] and with experimental data.[38-40] The average absolute error is 1.9 kcal/mol. The average absolute deviation of the predicted fundamental vibrational frequencies for $\text{H}_2\text{Si}=\text{SiH}_2$, $\text{H}_2\text{Si}=\text{SiH}$, $\text{H}_2\text{Si}=\text{Si}$, and SiH_2 from the results reported by Ho et al.[33,34] is 52.9 cm^{-1} . The computed barrier heights are in accord with measured thermal activation energies.[39,40]

To date, we have carried out one dynamical study using the Si_2H_4 global potential.[41] Cross sections and thermal rate coefficients for $\text{SiH}_2 + \text{SiH}_2$ recombination, reaction R13A, have been computed using classical trajectory techniques. Thermally

averaged formation cross sections vary from 66.3 \AA^2 at 300 K to 28.7 \AA^2 at 1500 K. The corresponding thermal rate coefficients lie in the range $2\text{--}4 \times 10^{14} \text{ cm}^3/\text{mol-s}$ over this temperature range and exhibit a maximum at an intermediate temperature. The trajectory details indicate that the reaction exothermicity is primarily partitioned into the Si-Si stretch and the H-Si-H bending modes upon formation of Si_2H_4 . Energy transfer from the Si-Si stretch to the Si-H stretching modes is a relatively slow process occurring on a time scale of 10^{-12} s , which is about three to four times that observed in polyatomic molecules such as benzene.

We have recently reported a general method for analyzing the results of classical trajectory calculations to obtain rates of intramolecular energy transfer.[42] The method is based on the determination of the time dependence of the normal mode velocities by projection of the instantaneous Cartesian velocities onto the normal mode vectors. It is shown that the method obviates the need to arbitrarily define a "bond" or "mode" energy as a means of following the energy flow. Average mode energies are computed using the virial theorem. For a given potential surface, the results are exact within the framework of the classical approximation. As an example, the method was applied to the study of intramolecular energy transfer in 1,2-difluoroethane. Decay rates and pathways of energy flow for initial excitation of each of the 18 vibrational modes have been determined. From the results obtained from the time variation of the normal mode velocities, we have extracted a first-order, mode-to-mode energy transfer rate coefficient matrix. The mode-to-mode coefficients are shown to provide an excellent means of collating the energy transfer information.

Their values yield a quantitative description of the energy transfer rates and a clear picture of the relative importance of the available pathways for energy flow in the system. At the present time, the method is being applied to intramolecular energy transfer in disilane.

C. Heterogeneous Surface Processes

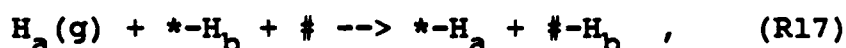
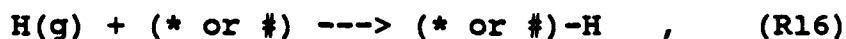
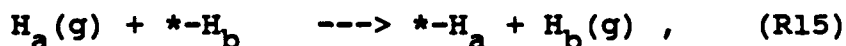
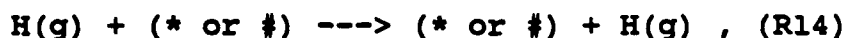
The surface processes of interest include inelastic surface scattering, sticking probabilities, dissociative chemisorption, surface diffusion, tunneling, and chemical reactions. To investigate these effects, we have made use of linear MCV PST methods adapted to the study of surface processes, WKB semiclassical methods coupled with MCV PST techniques, wave packet scattering, master equation type approaches, and classical trajectories where appropriate. Of particular interest, is the effect of surface temperature, surface orientation and reconstructions, surface dislocations and kinks, and surface coverage.

The problem of obtaining sufficiently accurate potential-energy surfaces is even more acute for heterogeneous systems than is the case for gas-phase reactions. Except for a few cluster calculations for selected systems, along with some thermodynamic and spectroscopic data, there is usually very little information available on the topographical features of these potential surfaces. Consequently, we must content ourselves with the use of more empirical surfaces. Such surfaces can be expected to yield at most qualitative, or in some cases, semi-quantitative, information related to the dynamics of these systems. This problem is analogous to the "surface" problem faced by experimentalists in this field who have great difficulty in characterizing and reproducing the physical surfaces under

study. Consequently, we regard our results as being indicators of the true system behavior, which is often unknown. Such "indicators" are useful in themselves and often point the way to new experiments or theoretical methods that will provide more accurate information.

Inelastic scattering, sticking, and dissociative chemisorption have been investigated for Si atoms, hydrogen atoms, molecular hydrogen and SiH_2 incident on Si(100) and Si(111) surfaces and partially/fully covered Si(111) surfaces.[43-47] Analogous studies on Si(111)-7x7 reconstructed surfaces are in progress. The lattice models used in these studies have 9 to 60 atoms in the primary reaction zone and 70 or more in the secondary or Q-zone. Either Weber's parametrization[48] of Keating's[49] potential or a potential recently developed by Brenner and Garrison[50] has been employed to represent the lattice interactions. To incorporate the effect of relaxation of the primary-zone atoms to the bulk phonon modes, we have developed a method using concepts analogous to those employed by Riley and Diestler[5] in their velocity reset method. Riley and Diestler have introduced relaxation effects by a periodic resetting of the velocities of a subset of particles which interact with the bath modes. In their method, the velocities are reset according to a prescription that involves the old velocity, a random velocity chosen from a Boltzmann distribution, and a reset parameter. Our procedure resets the velocities according to a prescription based on the local temperatures and the temperature of the bulk. Berendsen et al.[51] have shown that this method is equivalent to a Langevin procedure under conditions that all frictional coefficients are equal and there is no Gaussian white noise term.

The principal results obtained from the above studies are (1) sticking coefficients for Si atoms and SiH₂ molecules are near unity at all surface temperatures. (2) The major processes observed in collisions of hydrogen atoms with partially covered Si(111) surfaces are direct scattering, exchange scattering, direct chemisorption, and chemisorption with exchange, i.e.,



where * and # represent atop and open adsorption sites, respectively. (3) In the case of hydrogen atom adsorption on partially covered Si(111) surfaces, surface coverage is found to have only a small effect upon sticking probabilities. (4) Energy transfer to the surface is found to be a first-order process in which energy is transferred mainly from stretching motions of the adsorbate to the bending modes of the silicon surface. Rate coefficients for this transfer decrease with increasing surface temperature and are on the order of $1-2 \times 10^{12} \text{ s}^{-1}$.

(5) The nature of H₂ dissociative chemisorption of Si(111) surfaces is qualitatively similar to that observed by Wolken and coworkers for the H₂-W(100) system[52-55] and by Lee and DePristo [56-57] for H₂-Ni systems. The quantitative differences are mainly due to the increased exothermicity of H₂ chemisorption onto Si(111) caused by the dangling silicon bonds. H₂ adsorption in this system is always accompanied by dissociative chemisorption and the sticking probabilities are virtually independent of surface relaxation, the size of the lattice model, and the nature of the lattice potential. Si-H vibrational energy transfer rates to the lattice are increased and surface mobilities are decreased by the

inclusion of relaxation to bulk modes but the magnitude of these effects is less than a factor of two. (6) The results also include a detailed study of inelastic hydrogen atom scattering as a function of surface coverage and incidence angle.[47]

In addition to the above studies, we have also developed semiclassical wave packet methods that permit us to calculate diffraction patterns, surface phonon spectra, inelastic energy transfer, Debye-Waller factors, and surface desorption rates for atom-surface scattering.[58-60] We have most recently applied this method to the investigation of the relative contributions made by different surface phonon modes to the overall inelasticity of atom-surface collisions.[60]

Detailed studies of surface diffusion of Si atoms on Si(100) and Si(111) surfaces[59-61] and of hydrogen atoms on a clean Si(111) surface and on partially covered Si(111)[43,61,62] have been carried out. The silicon atom studies employ classical trajectories to compute jump frequencies between lattice sites which are then used to calculate thermal diffusion coefficients. Alternatively, we compute velocity autocorrelation functions or average mean square displacements from which diffusion coefficients may be extracted. These studies are patterned after the methods introduced by Doll and McDowell.[63,64]

If it is assumed that the jumps are uncorrelated and if there is only one type of adsorption site on the surface, the diffusion coefficient, D , is related to the jump frequency, k , by

$$D = L^2 k / 2d,$$

where d is the dimensionality of the diffusion and L is the jump length. If, however, there are two or more types of adsorption sites, the relationship between the various jump frequencies and the diffusion coefficient is not so simple. For such cases, we

have devised a master equation type approach that permits both upper and lower bounds to D to be computed directly from a knowledge of the various jump frequencies. The method has been applied to the case of silicon atom diffusion on Si(111) where there are two different types of adsorption sites.[62] By a comparison of the results of this method to diffusion coefficients computed from velocity autocorrelation plots, we have shown that the method yields very tight bounds on D .

Our results show that the activation energy for silicon atom diffusion on both unreconstructed Si(100) and Si(111) surfaces is between 3-5 kcal/mol. Experimental measurements of the diffusion rate have given activation energies varying from 4.6 to 58 kcal/mol.[65-68] Our results have allowed us to identify the lower value as the appropriate one for silicon atom diffusion on a terrace. Higher values are apparently due to the influence of steps and kinks in the experimental surfaces.

Classical hydrogen atom diffusion rates on a partially covered Si(111) surface have been computed using a variation of linear MCVPT methods.[69] Transition-state methods generally consist of computing the flux of systems across some dividing surface that completely separates the "reactant" and "product" states. Because of recrossings of the dividing surface, this flux is generally an upper limit to the true rate.[1] Chandler and coworkers[70] have described methods for incorporating dynamical corrections for recrossings and Voter and Doll[71] have extended the method to include treatment of many-state systems. In our procedure, we express the dividing surface as a linear combination of the configuration coordinates of importance in the dynamic process under consideration. The flux across the dividing surface is then minimized with respect to the expansion

coefficients to obtain a tight upper bound upon the true rate coefficient. We have previously shown that the method gives excellent results for gas-phase exchange reactions.[72]

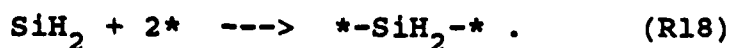
Most recently, we have obtained tunneling corrections to the hydrogen-atom diffusion coefficients on a partially-covered Si(111) surface.[69] The results show that diffusion is dominated by tunneling events even up to temperatures well in excess of 300 K. In addition, we find that phonon modes couple with the tunneling process and result in greatly enhanced tunneling rates. Similar results have previously been reported by Jaquet and Miller[73] and by Lauderdale and Truhlar[74] for hydrogen atom tunneling on W(110) and Cu(100) surfaces, respectively.

The theoretical study of surface chemical reactions is extremely difficult due to the lack of accurate potential-energy surfaces and to the large dimensionality of the problem. As a result, most such studies that have been reported to date deal with "simple" recombination on surfaces. We have carried out one such investigation, atomic hydrogen recombination on unreconstructed Si(111) surfaces, using linear MCV PST methods.[75] In addition, we have examined the mechanisms and rates for H_2 chemisorption[44,45] and the decomposition reactions of SiH_2 on Si(111) surfaces.[46] The H_2 chemisorption studies have been summarized above.

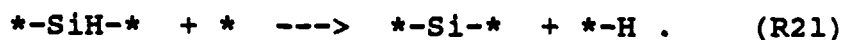
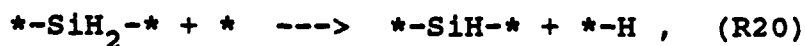
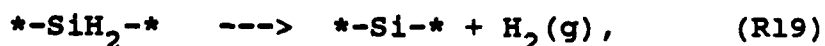
The variational phase space method used to calculate the H_2 recombination rate on a Si(111) surface is an extension of the linear variational methods we developed for the study of gas-phase reactions.[72] This method has recently been generalized by Koepl.[76] We have also introduced a procedure whereby the linear MCV PST method may be used to extract the minimum-energy

reaction path on a multi-dimensional hypersurface. The results of these studies are activation energies and frequency factors for the H_2 recombination. The calculated activation energies are in good accord with experimental results reported by Schulze and Henzler.[77] The frequency factors we obtain lie in between those obtained by Schulze and Henzler and values reported by Belyakov, Ionov, and Kompaniets[78] and by Brzoska and Kleint.[79]

Classical trajectories methods have been employed to examine the decomposition mechanisms and rates for SiH_2 reaction on a $Si(111)$ surface.[46] The primary adsorption mode is shown to involve tetrahedrally bonding of SiH_2 to two atop adsorption sites on $Si(111)$:



Subsequent decomposition pathways are direct H_2 elimination and sequential decomposition reactions in which the hydrogens bind to adjacent sites on the $Si(111)$ lattice:



The reactions are found to be first-order. The associated rate coefficients at 300 K are 0.35×10^{-12} , 1.9×10^{-12} , and $1.1 \times 10^{-12} \text{ s}^{-1}$, respectively. Consequently, the major decomposition pathway is the sequential elimination of atomic hydrogen to surface sites. Estimated barrier heights for reactions R19-R21 are 1.5, 0.51, and 0.24 eV, respectively.

We have recently published a general review of much of the above work.[80]

A perturbation-trajectory procedure for the investigation of the dynamics of gas-surface collisions has been developed. In

this method, the entire system is partitioned into a primary P-zone, a Q-zone, and sometimes, a boundary B-zone in a manner identical to that employed when using a generalized Langevin approach. It is assumed that the motions of the Q-zone atoms are unaffected by the collision process at the lattice surface. Under these conditions, the Q-zone motion can be obtained by direct solution of Hamilton's equations using a lattice Hamiltonian from which the interaction terms involving the incident molecule with the lattice have been omitted. This perturbation assumption yields the atomic coordinates of the Q-zone atoms as functions of time. Direct substitution of these functions into the system potential gives a time-dependent P-zone Hamiltonian from which the system behavior is computed using an ensemble of stochastic trajectories.

This method is similar to the lattice response function approach previously introduced by Barker and Steele[81] in that both methods incorporate the effect of the Q-zone atoms using the results of unperturbed lattice trajectories. The methods deviate primarily in the treatment of the P-zone lattice atoms. In the lattice response function method, approximate solutions for the motion of these atoms are obtained from the Laplace transforms of the lattice response functions and time-varying interaction forces using solutions valid only in the limit of complete separability of the lattice motion and interaction forces. The present method utilizes the numerically exact solution obtained from the P-zone Hamiltonian. In the limit where the P-zone contains no lattice atoms, the two methods become identical.

In the present perturbation-trajectory method, the effects of the Q-zone atoms upon the P-zone dynamics are included via the time-varying potentials that cause a net flow of energy

into or out of the P-zone. Thus, the Q-zone acts as a heat sink or reservoir just as it does in Langevin[82,83] and velocity reset[51,84-86] methods. However, in contrast to velocity reset methods and some Langevin studies, the present method retains the correct functional form for the P-zone - Q-zone interaction. In actual application, it is shown that this perturbation procedure is conveniently combined with other standard trajectory techniques to effect the required averaging over the dynamical variables describing the P and Q-zone motions.

Application of this perturbation procedure to collinear atomic collisions with a ten-atom chain shows that the accuracy of the method increases as the incident-to-lattice-atom mass ratio, the P-zone - Q-zone interaction, the initial incident-atom energy, or the total lattice energy decrease. Excellent results are obtained for incident-to-lattice mass ratios less than 0.1. In general, anything that tends to minimize the effect of the collision upon the Q-zone will increase the accuracy of the method. As expected, the method becomes increasingly accurate as the size of the P-zone is increased.

The perturbation method yields excellent results for the inelastic scattering of rigid-rotor NO from Ag(111) surfaces even for calculations in which the P-zone contains only the NO molecule. It is shown that the scattered distributions of rotational and total NO energies, as well as the calculated sticking probabilities and differential cross sections, agree almost exactly with those obtained from trajectory calculations using a 25-atom P-zone. Such agreement is not unexpected in view of the small nitrogen/silver mass ratio and the low thermal lattice energies present in the calculation. These results are shown to be in fair-to-excellent accord with previously reported

trajectory studies of this system that employ a six-atom P-zone and Langevin methods with approximate friction and fluctuating forces used to represent the effects of the rest of the lattice.[87] The quantitative differences between the two calculations are attributed to the small P-zones used in the Langevin studies[87] that fix the positions of ten of the lattice sites with which the NO is assumed to interact. In the present extended lattice and perturbation calculations, the motion of these lattice sites is explicitly considered.

It is found that larger P-zones are required to obtain good results from perturbation-trajectory studies in the reactive $\text{SiH}_2\text{-Si(111)}$ system. In this case, we find that perturbation results in which only the incident silylene radical is in the p-zone correctly predict the sticking probabilities and the major SiH_2 decomposition pathways but erroneously predict that Si, SiH_2 , and SiH desorption processes are highly probable. However, if a 12-atom P-zone is used, the results are nearly identical to those obtained in a complete treatment of the 28-atom system.

In general, we conclude that the trajectory-perturbation procedure will give excellent results for inelastic, light-atom collisions with heavy-atom surfaces at thermal temperatures. The stronger interactions involved in reactive events will usually require the use of larger P-zones but even in this case, a significant reduction in computational requirements will probably be realized.

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